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# An unexpected bridge between chemical bonding indicators and electrical conductivity through the localization tensor†

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While the modern theory of the insulating state shows that the conducting or insulating properties of a system can be extracted solely from the ground state properties via the so-called localization tensor (LT), no chemical reading of this important quantity has ever been offered. Here, a remarkable link between the LT and the bond orders as described by the delocalization indices (DIs) of chemical bonding theory is reported. This is achieved through a real space partition of the LT into intra- and interatomic contributions. We show that the convergence or divergence of the LT in the thermodynamic limit, which signals the insulating or conducting nature of an extended system, respectively, can be nailed down to DIs. This allows for the exploitation of traditional chemical intuition to identify essential and spectator atomic groups in determining electrical conductivity. The thermodynamic limit of the LT is controlled by the spatial decay rate of the interatomic DIs, exponential in insulators and power-law in conductors. Computational data of a few selected toy systems corroborate our results.

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## 1 Introduction

As the technological demand of smart, functional, or tailored materials increases, so does the need for understanding the basic physics behind their sought-after properties. In many cases this search has led to explore the new dimension that the dependence of physical properties on size introduces at the nanoscale. For instance, the predicted demise of Moore's law<sup>1</sup> has stirred up the development of new quantum-mechanically operated devices like the single electron transistor.<sup>2</sup> Similarly, new fields such as molecular electronics have become hot topics producing thousands of specialized papers.<sup>3</sup> Despite much work, the building of new physical or chemical intuition that may guide future research beyond that coming from brute force case-by-case simulations has proven to be much more difficult. In crystal engineering, as an example, although the situation is now much better than 20 years ago, we are still far from mastering the rules to synthesize on-demand crystal structures.<sup>4</sup>

Regarding electrical conductivity at the nanoscale, much work has been devoted in molecular electronics to quantitatively simulating electron transport in single-molecule junctions,<sup>5</sup> and some rules regarding the factors that govern their conductivity

have emerged. However, despite the efforts, no simple chemical rules linking the molecular structure and molecular conductivity have been found to date.<sup>3</sup> Since, in the end, all newly developed nanodevices depend on the chemical synthesis of tailored molecular fragments, we believe that finding simple chemical indicators of facile electronic transport or conductivity is an important goal with possibly major outcomes.

A guiding principle in this quest may be taken from the naïve chemical association between conductivity, and electron localization and delocalization. Key concepts in chemistry like conjugation, resonance, aromaticity, *etc.* are nothing but different incarnations of electron localizability. However, standard approaches coming from the theory of chemical bonding (TCB) are almost inevitably linked to the one-particle molecular orbital (MO) theory,<sup>6</sup> and molecular conductivity tends to be interpreted in terms of excitation gaps, *i.e.* HOMO–LUMO energetic differences, instead of as a ground state property that could be transformed into the sought conductivity indicators. Fortunately, a new paradigm in TCB has emerged in the last few decades<sup>7</sup> that defines (and explores) chemical objects in real space from orbital invariant densities (or density matrices). These techniques, collectively known as quantum chemical topology (QCT),<sup>8</sup> analyze the wave function of a system, and use meaningful fields to partition the physical space into regions or domains associated with: atoms, through the one particle density in the quantum theory of atoms in molecules<sup>7</sup> (QTAIM); cores, lone, and bonding pairs, through the electron localization function<sup>9</sup> (ELF) or the electron localizability indicator<sup>10</sup> (ELI), *etc.* Once the real space objects are

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defined, indicators are obtained at well-defined points, usually the critical points of the defining field, and the global expectation values of operators are divided into domain contributions. This allows, for instance, for a rigorous real space partitioning of the energy into intra- and interatomic components (the interacting quantum atoms (IQA) approach<sup>11</sup>) much in the spirit of the atomistic ansatz. QCT, well-known in quantum chemistry, is slowly entering condensed matter physics.

Early attempts that tried to link the conductivity features of a molecular system with its electron density failed.<sup>12</sup> This comes as no surprise, since conductivity leaves no simple scars on the density. Fortunately, QCT domain expectation values are based on physical observables, so QCT provides an open door to connect the physicist's and the chemist's intuitions, which tend to live in separate worlds. This is not easy to do in other TCB approaches. In this regard, a rigorous formalism coupling the insulating or conducting nature of an extended system with ground state properties exists.<sup>13</sup> Although not well known in the chemical literature, Kohn's theory of the insulating state does the job. It is electron (de)localization that explains conductivity, quantified by an object called the localization tensor (LT).

Thanks to QCT and its rigorous partitioning of quantum mechanical expectation values into atomic or functional group contributions, we find and explore here a remarkable bridge between the LT and the standard bond orders of chemistry, as defined in their real space manifestation known as delocalization indices (DIs). It is the rate at which bond orders decrease with the distance that determines whether a system will or will not be conducting in the static thermodynamic limit. Since we can examine straightforwardly the behavior of DIs among atoms or functional groups in several dimensions, we expect our results to be useful in building new conductivity chemical rules.

## 2 The modern theory of the insulating state and the assessment of conductivity *via* the localization tensor

A seminal work by W. Kohn in 1964<sup>13</sup> showed for the first time how the insulating nature of a system could be understood as a consequence of electron localization in the ground state, and not only from the properties of its excitation spectrum. However important, this line of reasoning remained largely unexplored until the end of the 1990's, when Resta revisited and generalized it.<sup>14–16</sup> As emphasized by this author,<sup>17</sup> it is the organization of electrons in the ground state that renders a system insulating or conducting. A central object that quantifies Kohn's localization in an  $N$  electron system is the localization tensor,  $\lambda$  or LT. It is defined as the second cumulant moment, per electron, of the total electronic position operator  $\hat{R} = \sum_i^N \hat{r}_i$ .

$$\lambda = \frac{1}{N} \left\{ \langle \Psi | \hat{R} \otimes \hat{R} | \Psi \rangle - \langle \Psi | \hat{R} | \Psi \rangle \otimes \langle \Psi | \hat{R} | \Psi \rangle \right\}. \quad (1)$$

We will use in this work bold fonts to indicate vectors or tensors, depending on the context, and the  $\otimes$  symbol for

tensor or cartesian products. As an example, the Cartesian components of the  $\mathbf{r} \otimes \mathbf{r}$  tensor are  $(\mathbf{r} \otimes \mathbf{r})_{\alpha\beta} = x_\alpha x_\beta$ .

One of the most important results of Resta's reformulation lies in the link between the behavior of  $\lambda$  in the thermodynamic limit and the electrical conductivity: the  $\lambda$  tensor, that measures the quadratic fluctuations of the polarization of the system, and that was initially used by Kudinov,<sup>18</sup> has a well-defined thermodynamic limit, diverging for conductors while remaining finite for insulators.

We will just provide, for consistency, a few ideas that may guide the informed reader about the origin of such a unique property. It stems from the fluctuation–dissipation theorem<sup>19</sup> that allows proving<sup>17</sup> first that

$$\lambda = \frac{\hbar}{\pi e^2 N} \int_0^\infty d\omega \text{Im} \alpha(\omega), \quad (2)$$

where  $\alpha(\omega)$  is the frequency dependent linear polarizability tensor. From this, if periodic boundary conditions are imposed, it can also be proven that

$$\lambda_{\beta\gamma} = \delta_{\beta\gamma} \frac{\hbar V}{\pi e^2 N} \int_0^\infty d\omega \frac{\text{Re} \sigma(\omega)}{\omega}, \quad (3)$$

with  $\sigma$  being the frequency dependent electric conductivity. For conducting systems, with non-vanishing  $\text{Re} \sigma$  at zero frequency, the diagonal components of  $\lambda$  diverge. These diagonal values can also be understood as localization lengths,<sup>19</sup> and they are related to the optical gap  $E_g$  by  $\lambda_{\alpha\alpha} \leq \hbar^2 / (2m_e E_g)$ .

Simple manipulations, already put forward by Resta,<sup>17</sup> allow recasting the LT in terms of the first order,  $\rho(\mathbf{r}_1)$ , and the second order,  $\rho_2(\mathbf{r}_1, \mathbf{r}_2)$ , spinless densities, which are also known as the electron density and the pair density, respectively:

$$\begin{aligned} \rho(\mathbf{r}_1) &= N \sum_{\sigma_i} \int d\mathbf{x}_2 \cdots d\mathbf{x}_N \Psi^* \Psi, \\ \rho_2(\mathbf{r}_1, \mathbf{r}_2) &= N(N-1) \sum_{\sigma_i} \int d\mathbf{x}_3 \cdots d\mathbf{x}_N \Psi^* \Psi. \end{aligned} \quad (4)$$

In the above expressions  $\Psi = \Psi(\mathbf{x}_1, \dots, \mathbf{x}_N)$  and we sum over all the  $\sigma_i$  spin components of the  $\mathbf{x}_i$  space-spin electron coordinates.

Using the exchange–correlation density, the part of the pair density containing the quantum mechanical effects due to the antisymmetry of the wavefunction,  $\rho_{xc}(\mathbf{r}_1, \mathbf{r}_2) = \rho(\mathbf{r}_1)\rho(\mathbf{r}_2) - \rho_2(\mathbf{r}_1, \mathbf{r}_2)$ , and defining the interparticle position vector  $\mathbf{r}_{12} = \mathbf{r}_1 - \mathbf{r}_2$ ,  $\lambda$  may be written in an explicitly origin independent, symmetrical form. As we show in the ESI,<sup>†</sup> after some algebraic manipulations,

$$\lambda = \frac{1}{2N} \int d\mathbf{r}_1 d\mathbf{r}_2 (\mathbf{r}_{12} \otimes \mathbf{r}_{12}) \rho_{xc}(\mathbf{r}_1, \mathbf{r}_2). \quad (5)$$

## 3 A bridge between conductivity and the theory of chemical bonding

Chemistry being the science of the interactions among electrons (or atoms, made from them and nuclei), it is not surprising that  $\rho_{xc}$ , which collects all non-classical behaviour in the pair-density, is emerging, slowly but steadily, as one of the pillars in the

modern TCB. Similarly, having shown that electrical conductivity is related to how electrons localize or delocalize, it is also expectable that the former is related to chemical bonding measures of electron delocalization. Undoubtedly, the latter have a rather long history in TCB.

In the present context, Bader and Stephens<sup>20</sup> already proposed in 1974 that the interatomic integration of  $\rho_{xc}$  measures the number of pairs of electrons shared between two atomic regions, and named this quantity the delocalization index (DI)

$$\delta^{AB} = 2 \int_A \mathrm{d}\mathbf{r}_1 \int_B \mathrm{d}\mathbf{r}_2 \rho_{xc}(\mathbf{r}_1, \mathbf{r}_2). \quad (6)$$

Here  $A, B$  are the spatial regions associated with the two atoms (or fragments) under scrutiny. A similar  $A, A$  integral, the localization index, determines the number of localized electrons in a region. The DI provides the fluctuations of the electron population in the  $A, B$  regions, also being a real space generalization of the standard MO Wiberg–Mayer bond order,<sup>21,22</sup> which physicists still use, in their majority, in its even cruder Mulliken flavor. In energetic terms, the interatomic exchange–correlation energy

$$E_{xc}^{AB} = \int_A \mathrm{d}\mathbf{r}_1 \int_B \mathrm{d}\mathbf{r}_2 \frac{\rho_{xc}(\mathbf{r}_1, \mathbf{r}_2)}{r_{12}} \quad (7)$$

has been shown to correspond to the covalent part of the interaction between the regions.<sup>23</sup> Besides these two direct links, a growing body of evidence shows the relevance of  $\rho_{xc}$ -based indices in TCB,<sup>24</sup> explaining facts as the nature of chemical interactions from DI profiles,<sup>24</sup> or rationalizing stereoelectronic effects.<sup>25</sup> As we are going to show, it is the innocent concept of bond order, a must in every freshman chemistry course, that stores information about electrical conductivity.

A couple of recent studies<sup>26,27</sup> had already started to show that DIs encode information about the insulating or conducting nature of a system through their spatial decay rate: in metals we find an algebraic oscillatory decline with the interatomic  $A-B$  distance, while in insulators their fall off is exponential. Consideration of strongly correlated cases<sup>27</sup> evidences that DIs are also suitable generalizations of the double occupation order parameter  $\mathcal{D}$  used in Hubbard models to signal metal–insulator transitions, and that they reveal how mesomeric effects in alternant hydrocarbons are deeply linked to the oscillatory pattern that leads to conductivity in the thermodynamic limit. An increase in the electron correlation strength (by increasing the Hubbard  $U/t$  parameter or equivalently by substituting carbon by heavier elements) eventually destroys the oscillations, pointing toward an active effect of electron correlation in chemistry, *e.g.* to smaller mesomeric effects in the heavier analogues of alternant hydrocarbons. Even more importantly, the decay of these indices may be followed along specific bond chains, directions, or along a combination of both. One needs to only choose appropriately the domains in the  $A, B$  pairs. This provides a quantitative tool in the discovery of low dimensional conductors.

### 3.1 The localization tensor in finite molecules

In the last few years, several works by Leininger, Evangelisti and coworkers<sup>28,29</sup> have examined the role of  $\lambda$  in molecular instead

of extended systems. To that end, these authors have preferred to use the total second cumulant, which they have called the total position-spread tensor,  $\Lambda$  or TPS, and not the per electron quantity. Even a spin resolved version has also been studied.<sup>30</sup>

It has been shown that the TPS is very sensitive to bond stretching, becoming large in the case of increased electron mobility. In simple diatomics, for instance, its parallel component is small at equilibrium, it increases as the interatomic distance is enlarged before achieving a maximum value close to the bond breaking region, and it decreases again towards the free atomic value at dissociation.

Although the TPS has been welcome, adding to the battery of new chemical bonding indicators at hand, its global character partially limits its applicability. Its evolution in a possibly complex process will just average out the total response of the system, even though some very restricted atomic or bond resolution might be achieved by following a particular component or projection that isolates an important direction in space. In order to become a useful TCB descriptor, this barrier needs to be overcome to understand the origin of convergence/divergence and the onset of conductivity as we approach the thermodynamic limit.

### 3.2 An atomic partition of the TPS

Being the expectation value of a two-electron operator, QCT offers an immediate solution to the problem: provided that a chemically meaningful division of the space exists, we can space partition  $\lambda$  or  $\Lambda$ , just as it is done in the IQA approach. Without loss of generality, we present an atomic partition of the TPS using the QTAIM. This can be made coarser (scaling it up to the functional group or molecular level) or finer (to the level of atomic core, bond and lone pair domains) at will. Another important point regards origin dependency, which may bring trouble in the partitioning if direct use of eqn (1) is made. This difficulty is eluded by using manifestly origin independent eqn (5).

Let us start with an exhaustive partition of the physical space  $R^3 = \bigcup A$  into atomic regions. A rigorous, physically sound possibility is provided by the QTAIM. Each of these regions or domains harbors a nucleus, at position  $\mathbf{R}_A$ . Given the one-to-one correspondence between domains and nuclei, we will label them interchangeably. Then,

$$\begin{aligned} \Lambda &= \sum_{A \geq B} \Lambda^{AB}, \\ \Lambda^{AA} &= \frac{1}{2} \int_A \mathrm{d}\mathbf{r}_1 \int_A \mathrm{d}\mathbf{r}_2 (\mathbf{r}_{12} \otimes \mathbf{r}_{12}) \rho_{xc}(\mathbf{r}_1, \mathbf{r}_2), \\ \Lambda^{AB} &= \int_A \mathrm{d}\mathbf{r}_1 \int_B \mathrm{d}\mathbf{r}_2 (\mathbf{r}_{12} \otimes \mathbf{r}_{12}) \rho_{xc}(\mathbf{r}_1, \mathbf{r}_2). \end{aligned} \quad (8)$$

Notice that the above expressions provide a chemical partition of the TPS (or the LT if we divide by  $N$ ).

The intra-atomic  $\Lambda^{AA}$  terms must tend to their free atomic values  $\Lambda_0^{AA}$  as the molecular system is pulled apart into atoms. Recalling that  $\int \mathrm{d}\mathbf{r}_1 \mathrm{d}\mathbf{r}_2 \rho_{xc}(\mathbf{r}_1, \mathbf{r}_2) = N$ , it is well known that the localization index of region  $A$ ,  $N_{AA} = \int_A \mathrm{d}\mathbf{r}_1 \int_A \mathrm{d}\mathbf{r}_2 \rho_{xc}(\mathbf{r}_1, \mathbf{r}_2)$ , defines the number of localized electrons in region  $A$ , so that

$\Lambda^{AA}$  measures the interelectron spread of these localized electrons in the atomic region, behaving grossly as  $\Lambda^{AA} \sim (N_{AA}/2)\langle r_{12}^2 \rangle_A$ . The intra-atomic contributions to the TPS are thus additive and size extensive, and their sum is clearly seen through this partition to provide a term that scales linearly with the size of the system (or the number of electrons) as we approach the thermodynamic limit. An important corollary is that the root of any divergence in the LT will not be found in these intra-atomic components (see below). As it happens with other intra-domain expectation values in QCT,  $\Delta\Lambda^{AA} = \Lambda^{AA} - \Lambda_0^{AA}$  reflects the local change in interelectron spread due to chemical bonding and, except in very specific cases, like those in which a large charge transfer occurs, we expect these  $\Delta\Lambda^{AA}$  values to be small.

The interatomic  $\Lambda^{AB}$  contributions are much more interesting, for they directly measure the change in the interelectron spread due to the delocalization associated with the formation (or breaking) of a particular bond. From chemical intuition, two spatially separated non-bonded atoms will display a vanishing  $\Lambda^{AB}$  value. Most, if not all, of the interesting behaviors of  $\Lambda$  are then to be found in these terms. Notice that when two separated entities interact, the  $\Lambda^{AA}$  components are non-vanishing at full-separation, changing upon interaction, but that the  $\Lambda^{AB}$  value is zero at infinite separation, sensing directly the interaction process.

### 3.3 How does $\Lambda^{AB}$ decay with distance?

Taking into account that  $A$  and  $B$  are two non-overlapping regions of space, the behavior of  $\Lambda^{AB}$  as the two centers move away from each other is determined by the decay rate of  $\rho_{xc}$  with the interelectron distance and the  $\mathbf{R}_{AB} = \mathbf{R}_A - \mathbf{R}_B$  distance itself. Provided that the two electron coordinates satisfy  $\mathbf{r}_1 \in A$  and  $\mathbf{r}_2 \in B$ , we may refer them to their local nuclear reference frames, respectively:  $\mathbf{r}_1 = \mathbf{R}_A + \mathbf{u}_1$  and  $\mathbf{r}_2 = \mathbf{R}_B + \mathbf{u}_2$ . With the above, the dependency of  $\Lambda^{AB}$  on the internuclear distance is explicitly separated. Let us define  $\mathbf{u}_{12} = \mathbf{u}_1 - \mathbf{u}_2$ , and the local integrals

$$\begin{aligned} I &= \int_A d\mathbf{u}_1 \int_B d\mathbf{u}_2 (\mathbf{u}_{12} \otimes \mathbf{u}_{12}) \rho_{xc}(\mathbf{r}_1, \mathbf{r}_2), \\ J &= \int_A d\mathbf{u}_1 \int_B d\mathbf{u}_2 \mathbf{u}_{12} \rho_{xc}(\mathbf{r}_1, \mathbf{r}_2), \end{aligned} \quad (9)$$

that may also be written in terms of spatial moments of the domain averaged Fermi holes introduced by R. Ponec,<sup>31</sup> which have been successfully used in the last few years to reveal many interesting effects in chemical bonding.<sup>32</sup> With these, we may write

$$\Lambda^{AB} = I + \mathbf{R}_{AB} \otimes J + J \otimes \mathbf{R}_{AB} + \frac{1}{2}(\mathbf{R}_{AB} \otimes \mathbf{R}_{AB})\delta^{AB}. \quad (10)$$

The first term contains only local distances, roughly decaying as  $\delta^{AB}$  itself, and out of the three remaining terms, the one leading the long-range behavior is the third. Thus, at large interatomic distances  $\Lambda^{AB} \sim (\mathbf{R}_{AB} \otimes \mathbf{R}_{AB})\delta^{AB}/2$ , and the parallel component of  $\Lambda$  along the bond direction will scale as

$$\Lambda_{\parallel}^{AB} \sim \frac{1}{2}\mathbf{R}_{AB}^2 \delta^{AB}. \quad (11)$$

This last important relation provides a new bridge between TCB descriptors in the ground state and the Kohn–Resta theory of the insulating state.

### 3.4 The chemical bonding origin of the convergence/divergence of $\lambda$

We can now turn to the convergence/divergence of  $\lambda$  in the thermodynamic limit. An explicit effective one-center expansion of  $\Lambda$  may be immediately written from our previous partition as

$$\Lambda = \sum_A \Lambda^A, \quad \Lambda^A = \Lambda^{AA} + \frac{1}{2} \sum_{B \neq A} \Lambda^{AB}. \quad (12)$$

Notice that the atomic additivity of  $\Lambda^A$  allows us to write

$$\lambda = \frac{1}{N} \sum_A \Lambda^A = \frac{N_{\text{at}}}{N} \langle \Lambda^A \rangle = \frac{\langle \Lambda^A \rangle}{n}, \quad (13)$$

where  $\langle \Lambda^A \rangle$  is the average of  $\Lambda^A$  over all the atoms comprising our system, and  $n$  is the average number of electrons per atom. The divergence of  $\lambda$  in the thermodynamic limit is equivalent to that of the average atomic-additive  $\langle \Lambda^A \rangle$ . Remarkably, the divergence of the LT can thus be nailed down to an atomic property.

Further analysis opens new avenues in understanding the onset of conductivity from a chemical perspective. Several paths may lead to a divergent  $\langle \Lambda^A \rangle$ . For instance, all the  $\Lambda^A$  terms may diverge themselves, or only one or a few. This analysis will identify essential and spectator atoms or functional groups in complex conducting systems. Essential groups for conductivity will be those for which  $\Lambda^A$  diverges, while spectator groups will be characterized by convergent  $\Lambda^A$ . We think that this classification scheme can help identify replaceable groups that will not change the basic conductivity properties of a system while tuning their fine conductive properties.

For each divergent  $\Lambda^A$ , our previous comments show that it will be the interatomic sum,  $\sum_{B \neq A} \Lambda^{AB}$ , not the intra-atomic  $\Lambda^{AA}$ ,

that will add to an infinite result. It is the interplay between the dimensionality of the system and the decay rate of  $\delta^{AB}$  that determines convergence. This binds the behavior of  $\lambda$  to the decay rate of DIs as already explored.<sup>26,27</sup>

To keep our discussion as simple as possible, we will now continue our reasoning in one-dimensional systems, where these ideas are most easily apprehended. In 1D, whenever  $\delta^{AB}$  decreases faster than  $\delta^{AB} \simeq \mathbf{R}_{AB}^{-d}$ , with  $d = 2$ , the  $\sum_{B \neq A} \Lambda^{AB}$  term will converge, and the contrary will make it diverge. Similarly, the limiting  $d$  exponent is 3, 4 for 2- and 3-dimensional conductivities to occur, respectively. These results perfectly match the findings relating the decay rate of the non-diagonal elements of the first order density in tight binding models of metals, as shown by Taraskin.<sup>33,34</sup> In contrast, exponentially decaying interatomic delocalization indices  $\delta^{AB}$  will always lead to insulating behavior, *i.e.* to convergent  $\lambda$  values. We would like to stress that the transition from exponential to power-law  $\delta^{AB}$  decay rates has already been found to occur in computational studies of model systems.<sup>27</sup>

The following expressions summarize the core of our findings in the thermodynamic limit:

- If  $\delta^{AB}$  decays exponentially with  $R^{AB}$ ,  $\lambda$  converges.
- In a  $d$ -dimensional system,  $\lambda$  converges/diverges if  $\delta^{AB}$  decays faster/slower than  $R_{AB}^{-(d+1)}$ . We propose that low-dimensional as well as bulk conductivity can be spotted by examining the behavior of  $\Lambda^{AB}$  along the appropriate directions, planes, or 3D regions, respectively.

## 4 Exemplifying the usefulness of the $\Lambda$ partition

We are now in a position to show the new insights at work in a few toy systems. We will first discuss two simple dissociation processes,  $\text{H}_2 \rightarrow \text{H} + \text{H}$  and  $\text{H}_2\text{O} \rightarrow \text{OH} + \text{H}$ , where we will see how, and why, the final localization of electrons in the products leads to a convergent  $\lambda$ , *i.e.* to insulating-like behavior. This will also make the essential role of electron correlation in correctly capturing the physics of the system. Finally, the early stages in the birth of a divergence, thus the switch towards metallic-like behavior, will be succinctly analyzed in a linear chain of equally spaced hydrogen atoms. The electronic structure calculations have been performed using the GAMESS package,<sup>35</sup> and the TPSs have been obtained for QTAIM atomic partitions through our PROMOLDEN<sup>36</sup> code, which is able to handle quite a number of correlated and non-correlated wave functions and several QCT partitions, not only the one provided by the QTAIM. Details of the implementation of the TPS in PROMOLDEN can be found in the ESI.†

### 4.1 The dissociation of $\text{H}_2$

First we discuss the  $\text{H}_2$  molecule ( $A = \text{H}$ ,  $B = \text{H}'$ ), a paradigm of covalent interactions. We have computed  $\Lambda$  at the Hartree-Fock (HF) and configuration active space (CASSCF) levels with the aug-cc-pVTZ basis set along with its dissociation coordinate. The results are presented in Fig. 1. Notice that the  $\Lambda$  tensor is diagonal in any reference frame in which the internuclear distance coincides with one of the coordinate axes, and that rotational invariance equalizes the other two orthogonal eigenvalues of  $\Lambda$ . We will call these two different components of  $\Lambda$   $\Lambda_{\parallel}$  and  $\Lambda_{\perp}$ , respectively. As already put forward by Resta<sup>17</sup> and Leininger *et al.*,<sup>28</sup> mean-field and correlated descriptions of the dissociation process differ essentially. Interestingly, these qualitative differences are also observed when the delocalization index is examined by itself.<sup>37</sup>

Failure to consider electron correlation leads to a parabolic divergence of  $\Lambda_{\parallel}$  as the internuclear distance increases. Its origin cannot be grasped by solely examining the full tensor, but its partitioning shows that, as expected, it is the interatomic component,  $\Lambda_{\parallel}^{AB}$ , that diverges. Through the eyes of our findings, the parabolic behavior is due to an artificial non-vanishing  $\delta^{AB}$  at infinite separation (the HF dissociation error). It may be instructive to recall that at the Hartree-Fock level we may write for closed-shell systems

$$\delta^{AB} = 4 \sum_{ij} S_{ij}^A S_{ij}^B, \quad (14)$$

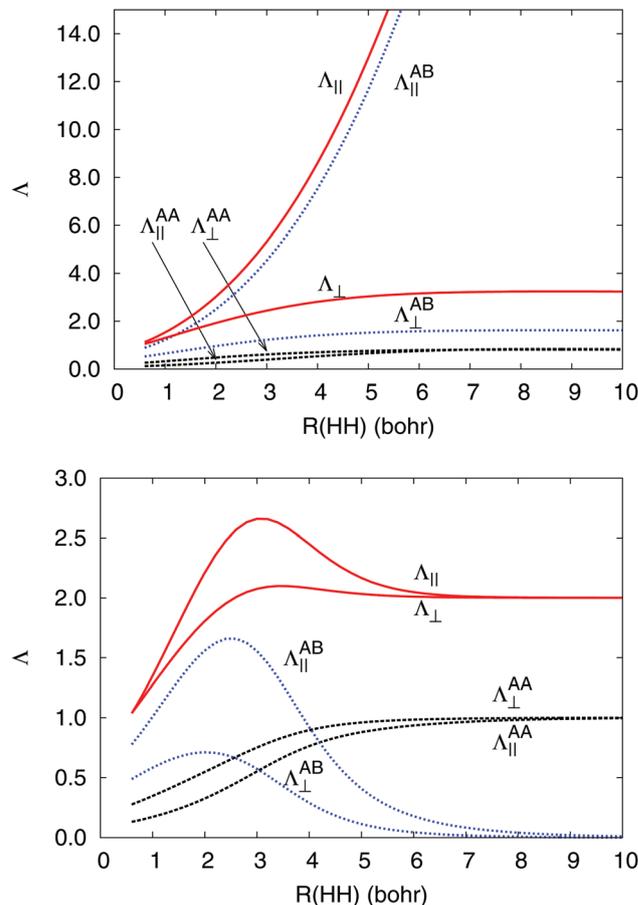


Fig. 1 Total, intra-atomic, and interatomic components of  $\Lambda$  in the  $\text{H}_2$  molecule at the HF (top) and CASSCF//aug-cc-pVTZ (bottom) levels along the internuclear dissociation coordinate. The parallel and perpendicular labels correspond to the internuclear and orthogonal directions, respectively. All data are in a.u.

where the sum runs over all pairs  $ij$  of occupied orbitals and  $S_{ij}^A$  is an atomic overlap integral

$$S_{ij}^A = \int_A d\mathbf{r} \phi_i(\mathbf{r}) \phi_j(\mathbf{r}). \quad (15)$$

As in  $\text{H}_2$  we have only one occupied HF orbital fulfilling  $S_{11}^A = S_{11}^B = 1/2$  by symmetry considerations, and the bond order  $\delta^{AB} = 1$  at any  $R_{\text{HH}}$  in this model. This can also be interpreted as a result of the two opposite spin electrons being statistically independent if no Coulomb correlation is added. The wrong constant  $\delta^{AB}$  leads to infinite-range delocalization, with an overall probability of finding the two electrons in any one of the H atoms (the so-called ionic weight in quantum chemical approaches) equal to  $1/2$ .<sup>38</sup> Eqn (11) does the rest.

Proper inclusion of Coulomb correlation makes  $\delta^{AB}$  decrease exponentially at large distances,<sup>39</sup> so that the bond breaks appropriately. Thus, in the correct correlated description, the intra-atomic  $\Lambda^{AA}$  components start at low values close to equilibrium, increasing to the free atom limit. From eqn (1), it is clear that in this limit  $\Lambda^{AA}$  is also diagonal and that each of its three components is equal to  $\langle \phi | r^2 | \phi \rangle$ , where  $\phi$  is the

hydrogenic atomic orbital in the state of interest. For the 1s ground state,  $\langle r^{-2} \rangle = 3$  a.u., so that  $\langle z^2 \rangle = 1$ , which is also the appropriate  $\Lambda^{AA}$  limit at dissociation.

Many other features of the behavior of the intra-atomic components are easy to rationalize. For instance, the lower value of  $\Lambda^{AA}$  at small interatomic distances is understood straightforwardly, for the number of localized electrons in each atom under these conditions is about 0.5, *vide supra*. It is also interesting to notice that the intra-atomic  $\Lambda_{\parallel}^{AA}$  value is smaller than its  $\Lambda_{\perp}^{AA}$  counterpart, reflecting the compression of the atomic density along the internuclear axis as we approach the two atoms from infinity. As also expected, it is the interatomic  $\Lambda^{AB}$  component that accounts for the sharp maximum in the total  $\Lambda$  tensor. This maximum has been interpreted<sup>28</sup> as a signature of bond breaking. Under our present formalism, it is a simple consequence of the shift from a power-law to an exponential decay in  $\rho_{xc}$  or  $\delta^{AB}$ , *i.e.* from a quasi-independent electron pair being stretched (as in the HF case) to the strongly correlated, localized dissociation limit. This transition, scaled by  $R_{AB}^2/2$ , gives rise to the maximum that is found very close to the internuclear distance at which the inflection point of  $\delta^{AB}$  has been repeatedly described.<sup>24,27</sup>

#### 4.2 The power of partitioning $\Lambda$ : $\text{H}_2\text{O} \rightarrow \text{OH} + \text{H}$

We can now show how the global behavior of  $\Lambda$ , that contains the total response of the system to a chemical process, may be split up into chemically meaningful terms. To that end we have chosen the  $\text{H}_2\text{O} \rightarrow \text{OH} + \text{H}$  dissociation, with the OH1 distance taken as an intrinsic reaction coordinate. Fig. 2 shows the evolution of  $\Lambda_{\parallel}^{AB}$  along  $R(\text{OH1})$  at the complete active space CASSCF[8,8]/aug-cc-pVTZ level. This exemplifies the power of partitioning  $\Lambda$ . As the OH1 distance is stretched, we see how there is a simple jump in  $\Lambda_{\parallel}^{\text{OH2}}$ , while it is  $\Lambda_{\parallel}^{\text{OH1}}$  that behaves much as in the  $\text{H}_2$  case. The step from lower to higher  $\Lambda_{\parallel}^{\text{OH2}}$  can be understood by taking into account that in the final OH radical the number of delocalized electrons between the O and the H2 atoms has increased. In other words, since the OH2

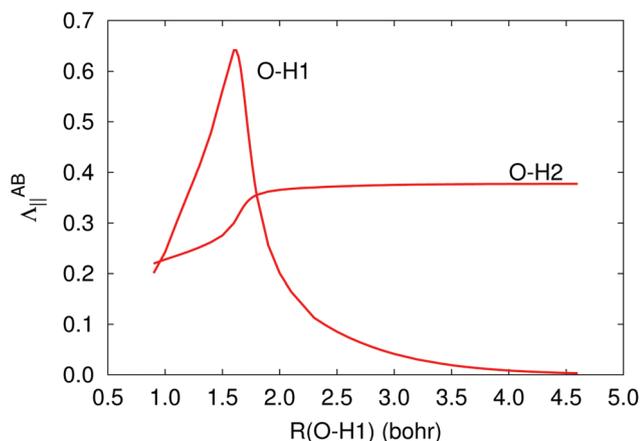


Fig. 2 Interatomic components of  $\Lambda_{\parallel}$  in the  $\text{H}_2\text{O}$  molecule at the CASSCF[8,8]/aug-cc-pVTZ level along the internuclear O–H<sub>1</sub> dissociation coordinate. All data are in a.u.

bond order increases as the H1 atom dissociates,  $\Delta\delta^{\text{OH2}} > 0$ , so does  $\Lambda_{\parallel}^{\text{OH2}}$ . Only a partitioning of the TPS, like the one devised here, will be able to isolate the main actors in complex scenarios. With our tools, this seems to be at hand, and the strong link between the essential interatomic  $\Lambda^{AB}$  terms and the DIs is unveiled.

#### 4.3 Recognizing the onset of conductivity: the $\text{H}_{10}$ chain

Our next example will be a linear chain of 10 equally spaced H atoms computed at the HF and full valence CASSCF levels with the 6-311G\* basis set. At the inter-hydrogen distance selected,  $R = 3.5$  Bohr, the HF model starts to fail, but it still provides a reasonable description of the electron system. We examine how the interelectron spread propagates along a quasi-1D system, and our goal is put on eqn (12). Fig. 3 shows how  $\Lambda_{\parallel}^{AB}$  changes for all pairs in which one of the atoms is fixed to be an end H. The first interesting point is that in the mean-field HF approximation,  $\Lambda_{\parallel}^{AB}$  decays with distance in a well-developed slow oscillatory pattern. We have found a similar behavior examining DIs.<sup>26,27</sup>

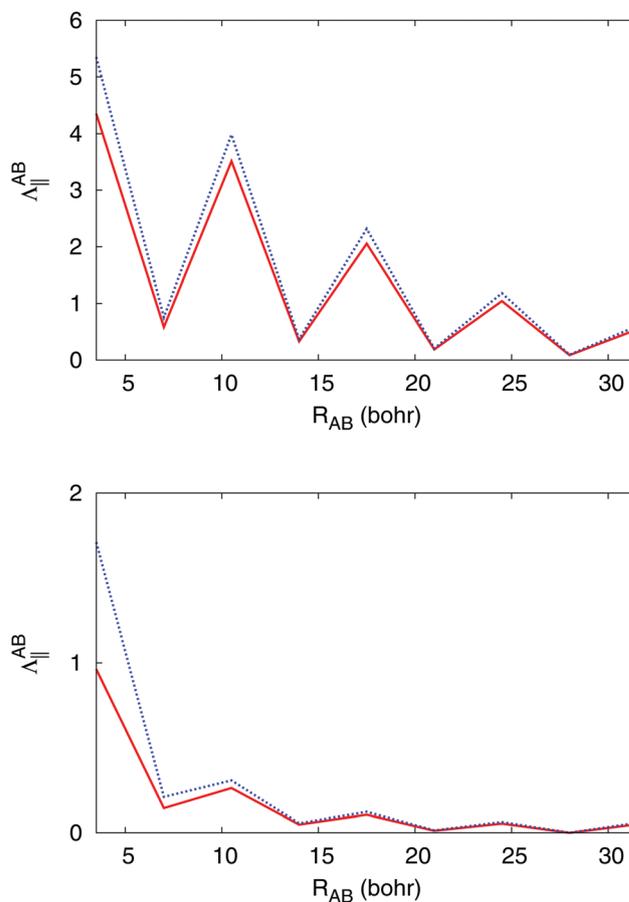


Fig. 3  $\Lambda_{\parallel}^{AB}$  along the internuclear direction in a  $\text{H}_{10}$  linear chain of equally spaced atoms at the HF//6-311G\* (top) and CASSCF//6-311G\* (bottom) levels. A labels one of the end H atoms, and B runs over all the others. Nearest neighbors are 3.5 Bohr apart. In each plot, the dashed curve corresponds to  $R_{AB}^2\delta^{AB}/2$ . All data are in a.u.

Notice that, from the chemical point of view, these oscillations signal a clear bond order alternation or mesomerism, precursor of a Peierls distortion (or  $H_2$  dimerization). This has also been repeatedly described in previous literature:<sup>24</sup> delocalization indices in geometrically constrained systems inform about the expected distortions when the constraints are released. As we find here, the localization tensor yields similar sensible chemical information.

A power law fit of  $\delta^{AB}$  to  $R_{AB}^{-d}$  gives  $d \approx 2.5$ , close to the tight binding value ( $d = 2.0$ ). The sum in eqn (12) achieves a very large value. The oscillatory pattern in  $\Lambda_{\parallel}^{AB}$ , as in the case of the DI, is a clear indicator of conducting-like behavior. A second point regards the very quick saturation of  $\Lambda^{AB}$  to the  $R_{AB}^2 \delta^{AB}/2$  leading term in the long range. Fig. 3 shows that our previous theoretical insights are fully realized from actual computations. It is the decay rate of DIs (*i.e.* the inter-center electron delocalization) that determines conductivity in the thermodynamic limit. Inclusion of electron correlation does not make the oscillations disappear at this interatomic distance, but reveals how the electrons are now much more localized, with a considerably smaller spread. A similar fit now gives  $d \approx 4.1$ , well above the metallic limit. We have shown that the oscillations

disappear when we enter the dissociating, localized regime, and that the DI decays exponentially in that case.<sup>27</sup>

#### 4.4 Insulating-like and conducting-like chains

We will finish our discussion by considering two real life one-dimensional linear chains of equidistant atoms:  $(LiH)_{15}$  and  $Li_{10}$ , with the nearest neighbor distances set to 3.0 and 5.818 bohr, respectively. We have used a HF/6-311G\* level that provides a simple, yet reasonable description for both systems. Fig. 4 shows relevant values for  $\Lambda_{\parallel}^{AB}$ , which provide clear grounds for comparison: the small values and the very quick decay of the interatomic  $\Lambda_{\parallel}^{AB}$  values in an insulator like lithium hydride, and their much larger magnitude, slow decay, and oscillatory behavior in the metallic-like chain.

## 5 Conclusions

In summary, we have shown in this article that a remarkable bridge exists between the Kohn–Resta theory of the insulating state, through the localization tensor (or its total position spread tensor version in molecular systems), and well known indicators used in the modern theory of chemical bonding as bond orders. This has been achieved by partitioning the localization tensor in intra- and interatomic components. An orbital invariant way to do so starts by writing the LT in terms of reduced densities and then partitioning the space into atomic regions according to quantum chemical topology. Convergence or divergence of the LT in the thermodynamic limit, associated with insulating or conducting electrical properties, depends exclusively on the decay rate of its interatomic components. The latter are dominated by the chemical delocalization index, a modern form of bond order. The chemistry of ground states and the physics of conductivity become intertwined in this way. We expect this new link to be useful in the search and design of low dimension conductors or insulators, for the total LT can be written as a sum of atomic (or functional group) components. Each atom or functional group in a system may thus be classified as essential, if its contribution to the LT diverges, or a spectator, if it converges, as electrical conductivity is regarded. We expect that this categorization can be used advantageously in the rational design of new materials.

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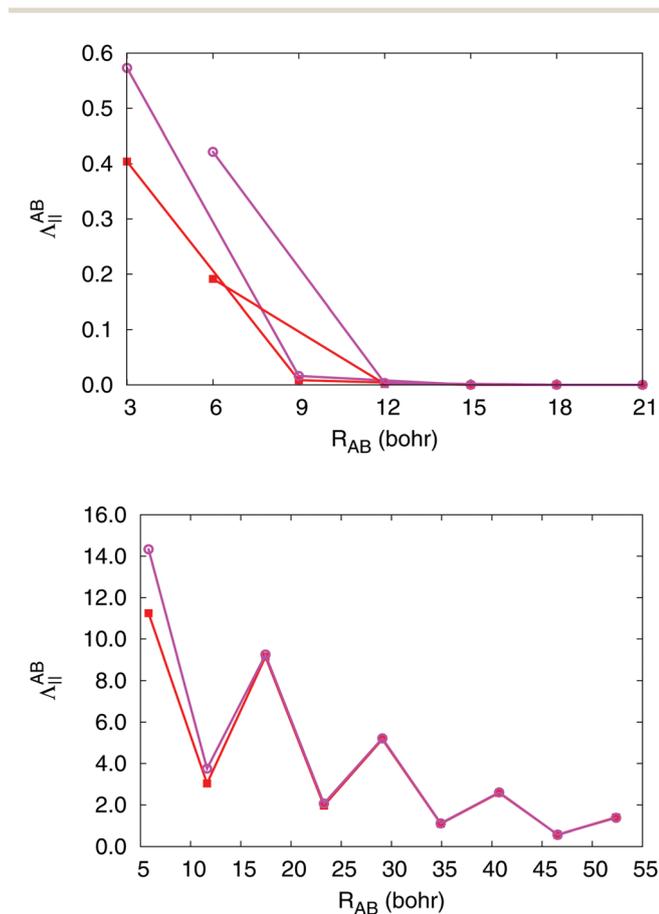


Fig. 4 HF/6-311G\*  $\Lambda_{\parallel}^{AB}$  (bold squares) and  $R_{AB}^2 \delta^{AB}/2$  (circles) along the internuclear direction. Top: Linear  $(LiH)_{15}$  chain of equally spaced nearest-neighbor atoms. Values starting at  $R_{AB} = 3.0/6.0$  Bohr correspond to the  $AB = LiH/HH$  pairs, respectively. Bottom: Linear  $Li_{10}$  chain of equidistant Li atoms separated by 5.818 Bohr. The  $AB$  pairs are those formed by one end Li atom and all its neighbors.

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